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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01L 21/306, C09G 1/02

A1

(11) International Publication Number: WO 95/24054

(43) International Publication Date: 8 September 1995 (08.09.95)

(21) International Application Number: PCT/US95/02793

(22) International Filing Date: 28 February 1995 (28.02.95)

(30) Priority Data:
08/203,786 1 March 1994 (01.03.94) US

(71) Applicant: RODEL, INC. [US/US]; 451 Bellevue Road, Newark, DE 19713 (US).

(72) Inventors: BRANCALEONI, Gregory; 107 Four Seasons Drive, Newark, DE 19702 (US). WANG, Jiun-Fang; 5 White Briar Circle, Hockessin, DE 19707 (US).

(74) Agent: BENSON, Kenneth, A.; P.O. Box 191, Chatham, PA 19318 (US).

(81) Designated States: CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: IMPROVED COMPOSITIONS AND METHODS FOR POLISHING

(57) Abstract

A composition is provided for polishing dielectric/metal composites, semiconductors and integrated circuits which contains an iodate compound. The iodate oxidizer may be used along with a compound or compounds which suppress the removal of the dielectric silica in the composite to provide an excellent selectivity of metal versus silica removal.

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IMPROVED COMPOSITIONS AND METHODS FOR POLISHING

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to the polishing of metals, dielectric/metal composites, semiconductors and integrated circuits. More particularly, this invention relates to improvements in the surface preparation of composite materials where improved polishing rates of metallic components is desired.

Description of the Related Art

Conventional polishing compositions or slurries generally consist of a solution which contains abrasive particles. The part, or substrate, is bathed or rinsed in the slurry while an elastomeric pad is pressed against the substrate and the pad and substrate are moved relative to each other. Thus the abrasive particles are pressed against the substrate under load and the lateral motion of the pad causes the abrasive particles to move across the substrate surface, resulting in wear, volumetric removal of the substrate surface.

In many cases the rate of surface removal is determined solely by the degree of applied pressure, the velocity of pad rotation and the chemical activity of the slurry particle. Enhancement of the chemical activity of the

polishing particle has been the basis of numerous patents, for example U.S.Patent No. 4959113 and U.S.Patent No. 5382272 both assigned to Rodel, Inc., Newark, Delaware.

An alternative means of increasing polishing rates is to add components to the slurries which by themselves are corrosive to the substrate. When used together with abrasive particles, substantially higher polishing rates may be achieved. This process, often termed chemical-mechanical polishing (CMP) is a preferred technique for polishing of semiconductors and semiconductor devices, particularly integrated circuits. Often they teach the introduction of additives which accelerate dissolution of the metal component in the polishing of dielectric/metal composite structures such as interconnect vias in integrated circuit structures. The purpose of this and other related techniques is to preferentially remove the metal portion of the circuit so that the resulting surface becomes coplanar. This process is ordinarily termed planarization.

It is highly desirable to improve the selectivity of metal planarization as much as possible. Carr et al. (U.S.Patent No. 4,954,142) teach improvements in CMP planarization of dielectric/metal composite structures by addition of a chelating agent to the slurry which is selective for the metal component of interest. This results in a further increase of the corrosion rate of the metal phase and increased selectivity of metal

versus dielectric phase removal, making the planarization process much more efficient.

Several other patents show chemical-mechanical polishing of a metal or metal containing layers on semiconductor substrates using slurries which contain oxidizing agents along with other solubilizing chemicals. These are U.S.Patent No. 4,956,313, U.S.Patent No. 4,992,135 and U.S.Patent No. 5,209,816. In all of these hydrogen peroxide is the oxidizing agent described as being useful for converting the metal to an oxide which is then subject to the chemical and mechanical action of the polishing slurry.

Hydrogen peroxide is again mentioned as a metal oxidizer in polishing slurries which also contain a compound or compounds that limit the rate of removal of silica and silicates from the surface being planarized. This is disclosed in U.S.Patent No. 5391258 assigned to Rodel, Inc., Newark, Delaware which is made part of this specification by reference.

There are disadvantages to using hydrogen peroxide, thus, alternative oxidizers are actively being sought. Hydrogen peroxide decomposes with time resulting in a slurry whose activity is decreasing. Chlorine containing compounds are also not satisfactory because they are corrosive to the materials in the semiconductor surface. Any chlorine containing compounds must be carefully removed from the surface of the semiconductor wafer before further use. It is therefore an object of this invention to provide an

oxidizer for metals and metal containing compounds which will perform satisfactorily in polishing slurries for planarization.

SUMMARY OF THE INVENTION

The object of this invention has been achieved by providing a composition for polishing dielectric/metal composites, semiconductors and integrated circuits which contains an iodate compound. The iodate oxidizer may be used along with a compound or compounds which suppress the removal of the dielectric silica in the composite to provide an excellent selectivity of metal versus silica removal.

DESCRIPTION OF THE INVENTION

We have unexpectedly found that iodates such as potassium iodate and sodium iodate perform well as oxidizing agents in polishing slurries without showing the disadvantages of oxidizing agents previously known in the polishing art. We have particularly found that an aqueous slurry composed of abrasive particles, an iodate oxidizing agent and a compound which contains at least two acid groups and, where the pKa of the first dissociable acid is not substantially larger than the pH of the polishing slurry, performs well in the planarization of metal/dielectric composites such as integrated circuits.

One would expect that the oxidation of a metal surface and its subsequent removal rate when polished using a slurry containing a given oxidant would be dependent on the reduction potential of the oxidant. Table 1 shows

the assumed half-cell reduction reactions and the standard reduction potentials (E^o) of some oxidants which have been used in compositions for tungsten polishing.

Table 1.

Reaction	E^o,Volts
$NO_3^- + 3H^+ + 2e^- <====> HNO_2 + H_2O$	0.934
$IO_3^- + 6H^+ + 6e^- <====> I^- + 3H_2O$	1.085
$ClO_4^- + 2H^+ + 2e^- <====> ClO_3^- + H_2O$	1.189
$H_2O_2 + 2H^+ + 2e^- <====> 2H_2O$	1.776
$S_2O_8^{2-} + 2H^+ + 2e^- <====> 2HSO_4^-$	2.123

EXAMPLE 1

Polishing compositions were prepared using a submicron alumina suspension to which were added water and reagent grade chemicals to make up formulations as shown in Table 2 below. Hydrochloric acid was added to each formulation to adjust the pH. These formulations were used to polish samples of sputter-coated tungsten metal film on Si substrates using identical conditions on a Strasbough 6DS planarizer.

Polishing conditions were:

Polishing pad:	Rodel IC1000
Pressure:	9psi
Platen Speed:	50rpm
Carrier Speed:	40rpm
Slurry Flow Rate:	200ml/min
Platen Temperature:	Ambient

The removal rate of tungsten was determined by weight loss of the tungsten sheet wafer.

Table 2.

Formulation	pH	Tungsten Removal Rate Angstroms/min
7%solids, 2%$Al(ClO_4)_3$	3.4	141
7%solids, 1%$K_2(S_2O_8)$	4.1	218
7%solids, 2%KIO_3	3.4	576

It is obvious from the data in Tables 1 and 2 that the removal rate of tungsten is not related to the reduction potentials of the oxidants used in the formulations and that it is indeed surprising that an iodate compound performs exceptionally well in formulations used for the polishing of tungsten.

EXAMPLE 2

A polishing composition was prepared as in Example 1 using a submicron alumina suspension. Added to the suspension were water, reagent grade potassium iodate and reagent grade potassium hydrogen phthalate to make a composition containing 7% solids, 3.2% potassium iodate and 4.4% potassium hydrogen phthalate. The pH of the polishing slurry in use is 4.1. This composition was used to polish samples of sputter-coated tungsten metal film on Si substrates and samples of thermally grown SiO_2 on Si substrates using identical conditions on a Strasbough 6DS planarizer. Polishing conditions were the same as those shown in Example 1.

The removal rate of tungsten was determined by weight loss of the tungsten sheet wafer. Removal rate for the oxide sheet wafers was determined using a Prometrix SM200/e film thickness measuring tool. The polishing rate of the tungsten metal was 1829 Angstroms/min while the polishing rate of SiO_2 was 84 Angstroms/min giving a selectivity of 22. This result compares very favorably with results obtained using fresh 50% hydrogen peroxide as the oxidizing agent in the slurry.

The preceding Examples show the efficacy of using slurries containing the formulations as shown and are not meant in any way to restrict the breadth of the invention as defined in the claims recited below.

CLAIMS

1. A polishing composition for substrates containing a metal and silicon dioxide comprising: an aqueous medium, abrasive particles ,an iodate compound and one or more compounds which suppress the rate of removal of said silicon dioxide wherein each of said compounds or compounds contains at least two acid groups and where the pKa of the first dissociable acid is not substantially larger than the pH of the polishing composition.

2. A polishing composition according to claim 1 in which said compound containing at least two acid groups is potassium hydrogen phthalate.

3. A polishing composition according to claim 1 in which said iodate is potassium iodate.

4. A polishing composition according to claim 1 in which said iodate compound is sodium iodate.

5. A polishing composition according to claim 3 in which said compound containing at least two acid groups is potassium hydrogen phthalate.

6. A polishing composition according to claim 4 in which said compound containing at least two acid groups is potassium hydrogen phthalate.

7. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 1 is used as the polishing slurry.

8. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 2 is used as the polishing slurry.

9. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 3 is used as the polishing slurry.

10. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 4 is used as the polishing slurry.

11. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 5 is used as the polishing slurry.

12. A method for polishing a substrate comprised of a metal and silicon dioxide in which a polishing composition according to claim 6 is used as the polishing slurry.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02793

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01L 21/306; C09G 1/02
US CL : US: 51/307; 106/3; 156/636,645,662,664,657; 252/79.1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : US: 51/307; 106/3; 156/636,645,662,664,657; 252/79.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,391,258 (BRANCALEONI ET AL) 21 FEBRUARY 1995	1-12
A	US, A, 3,429,080 (LACHAPELLE) 25 FEBRUARY 1969	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 10 MAY 1995	Date of mailing of the international search report 08 JUN 1995
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Form PCT/ISA/210 (second sheet)(July 1992)*